

CHROMATOGRAPHY OF SOME CATIONS BY MEANS OF PAPER TREATED WITH A LIQUID ANION EXCHANGER

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It is well known that anionic resins, such as IRA-400, Dowex-1, etc., have been used very successfully to retain and/or separate the cations that form anionic complexes with the most common acids. Hydrochloric acid forms chloro-complexes of different strength with the majority of cations; the behaviour of such complexes with anionic resins has been widely investigated and the adsorption curves have been reported for nearly every element of the periodic system¹.

Later, SMITH AND PAGE² found that when some amines are dissolved in organic solvents that are immiscible with water, they can be used to extract the anionic complexes of many cations from acid solutions, the behaviour of these amines being similar to that of liquid anion exchangers. Furthermore, long chain tertiary amines, such as tri-*n*-octylamine, tri-iso-octylamine, methyl-dioctylamine, etc., showed a good selectivity for the different cations.

As has been pointed out elsewhere, comparison of the data³⁻¹¹ published on the extraction of anionic complexes with anionic resins¹ with that on amines, shows that their behaviour is generally very similar.

Because of the great selectivity of these amines for many cations, it seemed worthwhile to investigate the possibility of applying them to paper-chromatographic separations.

Some interesting chromatographic separations were carried out by LEDERER¹²⁻¹⁴, who used papers impregnated with solid anion-exchange resins; these papers were obtained by dipping the chromatographic paper into a colloidal form of the resin. WITKOWSKI AND LEWANDOWSKI¹⁵⁻¹⁷ also prepared some papers impregnated with ion-exchange resins; later PETERSON¹⁸ separated uranium from bismuth with ion-exchange papers impregnated with IRA-400 and IR-45, as directly furnished by Rohm and Haas Co. KEMBER¹⁹ and KNIGHT²⁰ obtained some interesting results with a chemically modified cellulose: the papers were prepared from cotton fabrics that had been treated either with urea phosphate or with 2-aminoethyl sulphuric acid.

However, all these methods involve solid resins, and are sometimes rather tedious; furthermore the wet strips are generally weak and difficult to handle. It was therefore our aim to develop a reliable and simple method in which the chromatographic paper was treated with an amine solution.

EXPERIMENTAL

*Circular paper chromatography**Hydrochloric acid as eluting agent*

In order to get rapid and clear results, circular chromatography was used. From 0.02 to 0.05 ml of hydrochloric solution containing 20 to 50 μg of cations was deposited at the center of a paper disc (Whatman No. 1) with a diameter of about 10 cm. When the spot was completely dry, the paper was immersed in a solution of tri-*n*-octylamine (Fluka Co.) 0.2 *M* in kerosene 30–50°, and after elimination of the excess of the solvent with warm air, it was placed horizontally on the top of a glass crystallizing dish. The spot was then eluted by slowly dropping the acid on the centre of the disc with the aid of a very thin capillary tube. When the diameter of the wet surface was 7–8 cm, the paper was dried with warm air and then the different elements were developed with their specific reagents. In this manner it was possible to separate two or more elements in 15–20 minutes, and to obtain many indications for a preliminary investigation.

From the adsorption curves given in ref.¹ it can be seen that there are great differences in the behaviour of iron, cobalt and nickel in hydrochloric acid solutions. Therefore an attempt was made to separate the three elements by means of the above-mentioned technique using 4 *N* HCl. As expected on the basis of the considerations mentioned above, nickel actually followed the solvent front, not being complexed by the hydrochloric acid and therefore not retained by the amine; cobalt gave an R_F of 0.5 because of its partial complexation, whilst iron was completely complexed and therefore retained by the amine at the centre of the paper (Table I). A blank with a paper not treated with the amine did not show any separation, the three elements being found together at the solvent front ($R_F = 1$).

TABLE I
SEPARATION OF Fe^{3+} – Co^{2+} – Ni WITH 4 *N* HCl

<i>Element</i>	E_a^0 (from ref. ¹)	R_F	<i>Developer</i>
Fe^{3+}	1000	0	KCNS
Co^{2+}	< 1	0.50	8-Hydroxyquinoline
Ni	0	0.97	Dimethylglyoxime

Thus, by means of this chromatographic procedure, it is possible to separate two or more elements on the basis of the indications given by the adsorption curves of the anionic resins, that is by eluting the spots with a hydrochloric acid solution of suitable molarity. As a consequence of the treatment with the amine solution, the paper behaves like an anionic resin film, with the advantage that it is possible to develop the spots as in normal paper chromatography. Thus alkali metals, alkaline earth metals, aluminium, rare earths, yttrium, scandium, actinium, thorium, titanium, nickel, etc., can be separated from every element that gives complexes with hydrochloric acid. Generally the following rule holds: $R_F \rightarrow 0$ when $E_a^0 \rightarrow \infty$, and $R_F \rightarrow 1$ when

$E_a^0 \rightarrow 0$, where E_a^0 is the distribution coefficient of the anionic resin, or better, the extraction coefficient of the amine.

The separations obtained with the procedure described above are summarized in Tables I-X; the E_a^0 values are taken from the paper of KRAUS AND NELSON¹.

TABLE II
SEPARATION OF U^{6+} -Zr-Th WITH 10 N HCl

Element	E_a^0	R_F	Developer
U^{6+}	1000	0	$K_4Fe(CN)_6$
Zr	100	0.35	Quercetin
Th	0	0.95	8-Hydroxyquinoline

In the same manner as for the separation of U^{6+} -Zr-Th (Table II) it was possible to separate U^{6+} -Zr- Ti^{4+} ; in fact titanium (developed with hydrogen peroxide) showed an R_F value of 0.85.

Table III shows that the separation of copper from iron and aluminium becomes better if the molarity of the acid is increased from 1 to 1.5, in which case copper is more easily complexed and retained by the amine.

TABLE III
SEPARATION OF Fe^{2+} -Cu-Al WITH 1-1.5 N HCl

Element	E_a^0	R_F (1 N HCl)	R_F (1.5 N HCl)	Developer
Fe^{2+}	10	0	0	$K_4Fe(CN)_6$
Cu	< 1	0.80	0.42	$K_4Fe(CN)_6$
Al	0	0.98	0.98	Alizarin

The separation of U^{6+} - V^{5+} - Ti^{4+} is reported in Table IV, and the separations involving zinc, cobalt, manganese and nickel in Tables V-VII.

Furthermore, Cr^{6+} and Fe^{3+} can be separated from Al, and Fe^{3+} from Cr^{3+} , with 1-12 N HCl; in fact the R_F value for Cr^{6+} and Fe^{3+} is about zero, and that for Al and Cr^{3+} about 1 at every molarity of the acid.

TABLE IV
SEPARATION OF U^{6+} - V^{5+} - Ti^{4+} WITH 3 N HCl

Element	E_a^0	R_F	Developer
U^{6+}	> 10	1	$K_4Fe(CN)_6$
V^{5+}	< 1	0.38	Hydrogen peroxide
Ti^{4+}	0	0.95	Hydrogen peroxide

TABLE V
SEPARATION OF Zn-Mn²⁺ WITH 3 N HCl

Element	E_a^0	R_F	Developer
Zn	> 100	0.33	8-Hydroxyquinoline
Mn ²⁺	0	0.96	8-Hydroxyquinoline

TABLE VI
SEPARATION OF Zn-Co²⁺-Mn²⁺(Ni) WITH 4 N HCl

Element	E_a^0	R_F	Developer
Zn	> 100	0.15	8-Hydroxyquinoline
Co ²⁺	< 1	0.45	8-Hydroxyquinoline
Mn ²⁺	≤ 1	0.82	8-Hydroxyquinoline
(Ni)	0	0.97	Dimethylglyoxime

TABLE VII
SEPARATION OF Zn-Mn²⁺-Ni WITH 10 N HCl

Element	E_a^0	R_F	Developer
Zn	> 10	0.17	8-Hydroxyquinoline
Mn ²⁺	< 10	0.30	8-Hydroxyquinoline
Ni	0	0.96	Dimethylglyoxime

The chromatographic method described here was successfully used also to separate zirconium and hafnium in spite of the difficulty of separating these so similar elements. A solution of 8 N HCl containing 5 % conc. HNO₃ was used as eluting agent, and quercetin as developer. This type of solution had given very good separation factors for Zr and Hf in the extraction with tri-*n*-octylamine¹¹. In the experiments, zirconium and hafnium were first considered separately, and afterwards together. The experimental results are reported in Table VIII.

TABLE VIII
SEPARATION OF Zr AND Hf WITH 8 N HCl + 5 % CONC. HNO₃

Element	E_a^0 (from ref. 11)	R_F	Developer
Zr	> 2	0.25	Quercetin
Hf	< 0.01	0.80	Quercetin

From the data given so far it is clear that many interesting chromatographic separations can be carried out by this simple method, provided a suitable eluting agent can be found.

Sulphuric acid as eluting agent

Tertiary amines have also been very successfully used to extract uranium from sulphuric leaches²¹⁻²⁶, as only U^{6+} ($E_a^0 \sim 100$), Mo^{6+} ($E_a^0 \sim 1000$), Zr ($E_a^0 \sim 200$), and V^{5+} ($E_a^0 \sim 20$) are extracted in 0.1-1 *M* H_2SO_4 .

By using the chromatographic method described here, it was possible to separate U^{6+} from Fe^{3+} , Cu and Ni with 0.2 *M* H_2SO_4 , whilst Mo^{6+} was separated from the same elements with 0.5 *M* H_2SO_4 , as reported in Tables IX and X.

TABLE IX

SEPARATION OF U^{6+} FROM Fe^{3+} , Cu AND Ni WITH 0.2 *M* H_2SO_4

Element	E_a^0 (from ref. 24)	R_F	Developer
U^{6+}	> 100	0.08	$K_4Fe(CN)_6$
Fe^{3+}	< 0.1	0.66	$K_4Fe(CN)_6$
Cu	< 0.1	0.68	$K_4Fe(CN)_6$
Ni	< 0.1	0.97	Dimethylglyoxime

TABLE X

SEPARATION OF Mo^{6+} FROM Fe^{3+} , Cu AND Ni WITH 0.5 *M* H_2SO_4

Element	E_a^0 (from ref. 24)	R_F	Developer
Mo^{6+}	> 1000	0	8-Hydroxyquinoline
Fe^{3+}	< 0.1	0.85	$K_4Fe(CN)_6$
Cu	< 0.1	0.87	$K_4Fe(CN)_6$
Ni	< 0.1	0.97	Dimethylglyoxime

In the same way U^{6+} , Mo^{6+} , V^{5+} and Zr can be separated from any other element.

*Descending chromatography**Hydrochloric acid as eluting agent*

Good results have also been obtained by descending chromatography. The only drawback in our laboratory trials was that the eluted spots and the solvent front were sometimes a little irregular. This trouble occurred especially when the amount of amine was too large, and the molarity of the eluting acid too low, but it was possible

TABLE XI

SEPARATION OF Fe^{3+} - Co^{2+} -Ni WITH 3 *N* HCl

Element	E_a^0	R_F	Developer
Fe^{3+}	100	0	$K_4Fe(CN)_6$
Co^{2+}	< 1	0.37	8-Hydroxyquinoline
Ni	0	0.89	Dimethylglyoxime

to eliminate it by treating the paper with an amine solution pre-equilibrated with the acid that was to be employed as eluting agent. The results of the different separations obtained by descending chromatography with HCl are summarized in Tables XI-XVIII.

TABLE XIII
SEPARATION OF Zn-(Co²⁺-Mn²⁺-(Ni)) WITH 3% HCl

Element	E_a	R_f	Developing
Zn	> 100	(0.03)	\$-Hydroxyquinoline
(Co ²⁺)	< 10	(0.44)	\$-Hydroxyquinoline
Mn ²⁺ -(Ni)	0	(0.90)	\$-Hydroxyquinoline ((dimethylglyoxime))

TABLE XIV
SEPARATION OF Fe²⁺-Cu AND Al WITH 2% HCl

Element	E_a	R_f	Developing
Fe ²⁺	100	(0.03)	$K_4Fe(CN)_6$
Cu	< 10	(0.27)	$K_4Fe(CN)_6$
Al	10	(0.90)	Alizarin

TABLE XV
SEPARATION OF U⁶⁺-Zr AND Th WITH 5% HCl

Element	E_a	R_f	Developing
U ⁶⁺	> 100	0	$K_4Fe(CN)_6$
Zr	< 10	(0.32)	Quercetin
Th	0	(0.82)	\$-Hydroxyquinoline

TABLE XVI
SEPARATION OF U⁶⁺-Zr AND Th WITH 5% HCl

Element	E_a	R_f	Developing
U ⁶⁺	> 100	0	$K_4Fe(CN)_6$
Zr	< 10	(0.32)	Quercetin
Th ⁴⁺	< 10	(0.76)	Hydrogen peroxide

TABLE XVII
SEPARATION OF U⁶⁺-Th⁴⁺ AND Th WITH 9% HCl

Element	E_a	R_f	Developing
U ⁶⁺	> 100	0	$K_4Fe(CN)_6$
Th ⁴⁺	> 10	(0.67)	Hydrogen peroxide
Th	0	(0.82)	\$-Hydroxyquinoline

TABLE XVII
SEPARATION OF Zr-Ti⁴⁺-Th WITH 9 N HCl

Element	E_a^0	R_F	Developer
Zr	> 10	0.1	Quercetin
Ti ⁴⁺	> 1	0.67	Hydrogen peroxide
Th	0	0.82	8-Hydroxyquinoline

TABLE XVIII
SEPARATION OF U⁶⁺-V⁵⁺-Ti⁴⁺ WITH 3 N HCl

Element	E_a	R_F	Developer
U ⁶⁺	> 10	0.01	K ₄ Fe(CN) ₆
V ⁵⁺	< 1	0.69	Hydrogen peroxide
Ti ⁴⁺	0	0.90	Hydrogen peroxide

Finally, as can be seen in Table XIX, a good separation of zirconium and hafnium was also obtained with HCl containing some HNO₃.

TABLE XIX
SEPARATION OF Zr AND Hf WITH 8 N HCl + 5 % CONC. HNO₃

Element	E_a^0 (from ref. ²¹)	R_F	Developer
Zr	> 2	0.17	Quercetin
Hf	< 0.01	0.50	Quercetin

Sulphuric acid as eluting agent

Uranium and molybdenum were separated from iron, copper, and nickel by descending chromatography with sulphuric acid, as show in Tables XX and XXI.

TABLE XX
SEPARATION OF U⁶⁺ FROM Fe³⁺, Cu AND Ni WITH 1 M H₂SO₄

Element	E_a^0 (from ref. ²⁴)	R_F	Developer
U ⁶⁺	> 100	0.19	K ₄ Fe(CN) ₆
Fe ³⁺	< 0.1	0.56	K ₄ Fe(CN) ₆
Cu	< 0.1	0.58	K ₄ Fe(CN) ₆
Ni	< 0.1	0.76	Dimethylglyoxime

TABLE XXI
SEPARATION OF Mo⁶⁺ FROM Fe³⁺, Cu, AND Ni WITH 0.2 M H₂SO₄

Element	E_a^0 (from ref. ²⁴)	R_F	Developer
Mo ⁶⁺	> 1000	0.01	8-Hydroxyquinoline
Fe ³⁺	< 0.1	0.27	K ₄ Fe(CN) ₆
Cu	< 0.1	0.30	K ₄ Fe(CN) ₆
Ni	< 0.1	0.77	Dimethylglyoxime

CONCLUSIONS

The results of this work show that a chromatographic paper treated with tri-*n*-octylamine behaves like an anion exchanger, and that many separations that are possible with the aid of solid resins or liquid exchangers, can also be achieved with this type of chromatography.

Moreover, this technique provides a simple and rapid method for the isolation of traces of complexed elements from large quantities of other elements not retained by the amine. After a kind of "stripping" of the spot with dilute nitric acid, it is possible to determine the isolated element quantitatively. Thus, a few μg of iron were separated quantitatively from mg quantities of nickel by filtering the hydrochloric solution containing the two elements through a filter paper treated with tri-*n*-octylamine.

SUMMARY

Chromatographic paper treated with a liquid anion exchanger (tri-*n*-octylamine) behaves like an anionic resin film; consequently many separations of cations that form anionic complexes can also be carried out by means of this new chromatographic procedure. Many examples are reported, among which the separation of the very similar elements zirconium and hafnium is of great significance.

It is anticipated that it will be possible to isolate traces of complexed metals from large quantities of non-complexed elements.

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